Effect of external pressure on the Fe magnetic moment in undoped LaFeAsO from density functional theory: Proximity to a magnetic instability

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We investigate the effect of external pressure on the Fe magnetic moment in undoped LaFeAsO within the framework of density-functional theory and show that this system is close to a magnetic instability. The Fe moment is found to drop by nearly a factor of 3 within a pressure range of ±5 GPa around the calculated equilibrium volume. While the Fe moments show an unusually strong sensitivity to the spin arrangement (type of antiferromagnetic structure), the low-temperature structural distortion is found to have only a minor influence on them. Analysis of the Fermi-surface topology and nesting features shows that these properties change very little up to pressures of at least 10 GPa. We discuss the magnetic instability in terms of the itinerancy of this system.

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I. INTRODUCTION

The discovery of high-T_c superconductivity in fluorine-doped LaFeAsO (Ref. 1) with a critical temperature T_c of about 26 K has stimulated an enormous interest in these compounds. Shortly after this discovery it became clear that a whole family of related compounds shows superconductivity at elevated temperatures. Substitution of La by other rare-earth elements increases T_c up to about 50 K (Ref. 2) and superconductivity at 38 K was also observed in the related $K_{0.4}Ba_{0.6}Fe_2As_2$ compound.[3]

The undoped parent compound LaFeAsO is an antiferromagnet with a small ordered Fe moment of about $0.4\mu_B$.[4] Density-functional theory (DFT) calculations find, in contrast, a much too large value for the Fe moment close to $2\mu_B$. The failure of DFT calculations to describe the Fe magnetic moment in these systems has raised doubts whether the underlying electronic structure is correct and whether it provides a sound basis for discussion of the superconducting state in the doped compounds. We argue here that the discrepancies between experiment and theory have a physical origin, namely, the fact that LaFeAsO is close to a magnetic instability. Based on our DFT calculations we show that the Fe moment is highly susceptible to external pressure and drops by almost a factor of 3 within the pressure range from −5 to 5 GPa. This drastic change in the Fe moment goes along with only subtle changes in the electronic structure, which explains the initially apparent differences between DFT-calculated moments and experimental observations. The predicted changes in the Fe moment allow for direct experimental verification, by applying either hydrostatic pressure or negative pressure, which could be realized by hydrogenation.

The crystal structure of LaFeAsO is tetragonal at room temperature and consists of FeAs layers separated by LaO layers (Fig. 1). Below $T_s \approx 155$ K a weak structural distortion is observed, followed by the formation of a spin-density wave (SDW) state around $T_N \approx 137$ K.[4] The low-temperature crystal structure has been described as either monoclinic[4] or orthorhombic.[5] Both structures differ only marginally from each other, so that the symmetry can be described as orthorhombic (see supplement of Ref. 4). The antiferromagnetic (AF) order of most of the undoped parent compounds of the iron arsenide superconductors has led to speculations that spin fluctuations could be decisive for the pairing mechanism.[6] On the other hand, the absence of a SDW state has been reported for NdFeAsO, where AF order is only observed below 2 K and Fe orders together with the Nd moments.[7] A strong electron-phonon coupling of the Fe breathing mode in $LaFeAsO_{1-x}F_x$ was reported in Ref. 8, which could contribute to the high T_c. Thus, the pairing mechanism is still under debate and requires further experimental and theoretical studies.[9]

The effect of hydrostatic pressure on the magnetic and superconducting properties of the iron arsenide compounds has been extensively studied by experiments.[10–17] For fluorine-doped LaFeAsO, an increase in the superconducting T_c under pressure with a maximum value of 43 K around 4 GPa was reported.[10] For undoped AFe_2As_2 compounds (A=Ca, Sr, and Ba), which order antiferromagnetically at

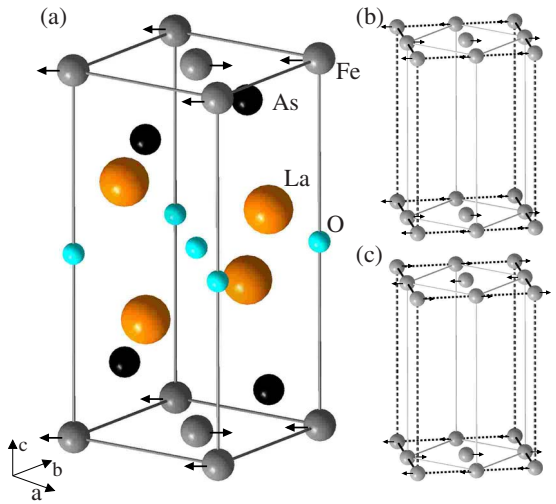

FIG. 1. (Color online) Crystal structure of LaFeAsO and spin arrangement of the three antiferromagnetic structures (a) AF1, (b) AF2, and (c) AF3 considered in the calculations. The unit cell for AF3 is doubled along the c direction.

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ambient pressure, pressure-induced superconductivity up to $T_c \approx 29$ K for A=Sr and Ba (Ref. 15) and up to $T_c \approx 12$ K for A=Ca (Refs. 13 and 14) was observed. Very recently, pressure-induced superconductivity was also reported for undoped LaFeAsO with a maximum value of $T_c \approx 21$ K around 12 GPa.[16]

II. COMPUTATIONAL DETAILS

We performed electronic structure calculations in the framework of DFT using two high-precision all-electron codes, the full potential local-orbital (FPLO) method[18] and the full potential linearized augmented plane wave (FLAPW) method implemented in WIEN2K.[19] To ensure that our conclusions do not depend on the choice of functional approximation to DFT, we employed both the local spin-density approximation (LSDA) and the generalized gradient approximation (GGA). Calculations were done for different volumes in the tetragonal crystal structure ($P4/nmm$), as well as in the orthorhombic crystal structure ($Cmma$), which are the crystal structures above and below T_s, respectively.

We considered three different types of AF spin arrangements (Fig. 1). The first cell (AF1) corresponds to a checkerboard arrangement in the original unit cell, where nearest-neighbor Fe atoms are aligned antiferromagnetically in the xy plane with a ferromagnetic (FM) stacking along the c axis. Second, we considered a stripelike spin arrangement in the plane with FM stacking along the c axis (AF2) in a $\sqrt{2} \times \sqrt{2} \times 1$ supercell. The third spin arrangement (AF3) has the same stripelike stacking in the plane as AF2, but in addition the spins are also arranged antiferromagnetically along the c axis in a $\sqrt{2} \times \sqrt{2} \times 2$ supercell. The experimentally observed spin arrangement[4] is AF3 and has so far not been addressed by electronic structure calculations.

For all calculations, the scalar relativistic approximation was used. The FPLO calculations (FPLO version 7.00-28) were performed in the LSDA in the parametrization of Perdew and Wang.[20] For the **k**-space integrations 512 **k** points in the full Brillouin zone (FBZ) were used for the structure optimization, and the convergence of the magnetic moments and Fermi-surface (FS) properties was checked with up to 32 768 **k** points in the FBZ. In the FLAPW calculations[19] the exchange-correlation functional is evaluated within the GGA, using the Perdew-Burke-Ernzerhof parametrization.[21] The muffin-tin radii for La, Fe, As, and O were chosen as 2.3, 2.15, 2.10, and 1.75 Bohr radii, respectively. Self-consistent calculations employed a grid of 4000 (AF1) and 2000 (AF2 and AF3) **k** points in the FBZ. $R_{\mathrm{MT}} \times k_{\max} = 7$ was used as the plane-wave cutoff.

III. RESULTS

A. Fe moment as a function of volume

As a first step, we consider the magnetic properties of LaFeAsO as a function of volume in the tetragonal structure, with the free parameters c/a, z_{As}, and z_{La} fixed initially to their experimental ambient pressure values.[4] This allows us to distinguish between the effects of different spin arrangements, structural parameters, and the influence of the exchange and correlation functional. Early electronic structure calculations (see Ref. 22 for an overview) showed a confusing variety of results for the magnetic properties of LaFeAsO, with values for the calculated Fe moment between almost 0 and $2.6\mu_B$. It soon turned out that the Fe moment is highly sensitive to the functional as well as the details of the structure and the spin arrangement used in the calculations.[22,23] While calculations assuming a FM alignment of the spins yield magnetic moments of $\approx 0.3\mu_B$ (almost in accidental coincidence with experiment), calculations using the correct AF spin arrangement obtain Fe moments substantially larger than the measured $\approx 0.4\mu_B$.

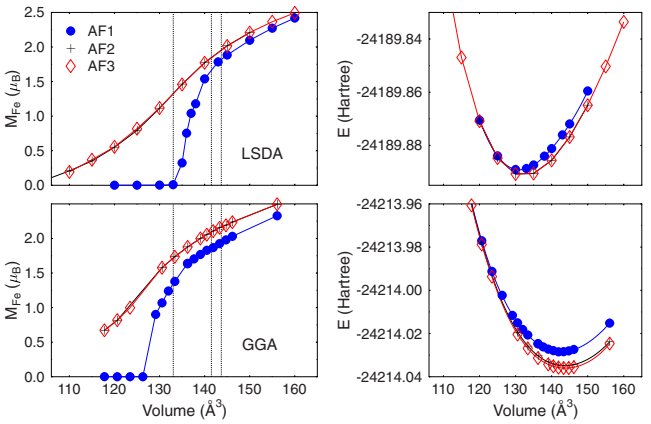

FIG. 2. (Color online) Left: Fe moment as a function of volume (top: LSDA; bottom: GGA) with c/a, z_{As}, and z_{La} fixed to their experimental ambient pressure values for different types of AF spin arrangement (see text). Dashed vertical lines denote the calculated LSDA equilibrium volume, the experimental volume, and the calculated GGA equilibrium volume (from left to right). Right: corresponding total energies.

The variation in the Fe moment and the total energy as a function of volume for the three different spin arrangements is shown in Fig. 2. The calculated Fe moment for the stripelike spin arrangements AF2 and AF3 at the experimental lattice parameters is $1.87\mu_B$ within LSDA. The corresponding magnetic stabilization energy with respect to the nonmagnetic state is 3.2 mHartree per Fe, in good agreement with the results obtained by Mazin *et al.*[22] In agreement with experiment, the stripelike spin arrangement is lowest in energy. Since the magnetic coupling between different Fe layers along the c axis is weak, AF2 and AF3 are very close in energy and have also similar electronic structure and magnetic moments, which justify the use of the AF2 structure in earlier calculations.

Although the three AF structures have similar Fe moments at the experimental lattice parameters, their behavior with respect to small changes in the volume is remarkably different. While the Fe moment of the checkerboard arrangement AF1 sharply drops with decreasing volume and vanishes already close to the calculated LSDA equilibrium volume, it decreases more smoothly for the stripelike arrangements AF2 and AF3. The GGA calculations (Fig. 2, bottom) show qualitatively the same behavior, which rules out that the observed behavior is due to a special property of a certain functional. Within GGA, the Fe moments and mag-

netic stabilization energies ($2.11\mu_B$ and 6.6 mHartree at the experimental lattice parameters) are higher than in LSDA, as expected from the well-known tendency of GGA to overestimate magnetic interactions.

The remarkable sensitivity of the Fe magnetic moments on the type of AF spin arrangement and structural details shows already that LaFeAsO is on the verge to a magnetic instability with respect to changes in the volume. In the vicinity of a magnetic transition or instability, parameter-free LSDA or GGA calculations cannot be expected to yield the exact value for the magnetic moment, but they should qualitatively reproduce the behavior as a function of an external parameter such as pressure. However, the results shown so far do not yet fully explain the deviations between the calculated and measured Fe moments. While a sharp drop as in the case of AF1 could well explain those deviations, the Fe moments remain substantially too large in the vicinity of the equilibrium volume for the correct AF3 spin structure.

B. Structural optimization: Fe moment as a function of pressure

Our next step is to consider structural optimizations of the free parameters c/a, z_{As}, and z_{La} for different volumes. In earlier publications it was pointed out that the magnetic moments in LaFeAsO are highly sensitive to structural parameters, especially to the height of the As position z_{As}.[22,24] Under pressure, changes in the structural parameters with respect to their ambient pressure values can be expected. In the following we restrict ourselves to LSDA calculations, which are better suited to describe the magnetic behavior in the vicinity of a magnetic instability due to the tendency of GGA to overestimate the magnetic interactions. LSDA calculations have, for example, successfully been used to predict a metamagnetic transition in YCo_5 under pressure.[25]

The structural optimizations have been performed with spin-polarized calculations in the AF3 structure. The c/a ratio shrinks considerably with pressure, reflecting a weak interlayer coupling, and also the internal parameters are subjected to considerable changes (inset of Fig. 3). The Fe moment, calculated with the optimized parameters as a function of pressure, is shown in Fig. 3. Within ± 5 GPa around the calculated equilibrium volume (zero pressure), the Fe moment drops by nearly a factor of 3. The calculated moment at zero pressure is $0.75\mu_B$ and thus still about two times larger than the experimental value. At a pressure of about 5 GPa, the calculated Fe moment coincides with the one observed in experiments. The magnetic stabilization energy decreases from 2.6 mHartree per Fe at -10 GPa to about 0.3 mHartree per Fe at ambient pressure. Spin fluctuations, which are only incompletely included in LSDA or GGA calculations, are expected to lead to a substantial suppression of the magnetic moment when the magnetic stabilization energy is of the order of 0.5 mHartree per atom.[22] Hence, an even sharper reduction in the Fe moment with pressure than the one shown in Fig. 3 might be observed in experiment, although the precise effect of the spin fluctuations cannot be estimated.

Up to now, we did not consider the effect of the orthorhombic lattice distortion observed at low temperatures. We find indeed a minimum in the total energy with a small deviation in the b/a ratio of about 1% from a tetragonal lattice, in agreement with experiment and an earlier report by Yildirim.[26] However, in contrast to the work of Yildirim[26] we find only a minor influence of this orthorhombic distortion on the Fe moments ($\approx 0.05\mu_B$), leaving the data shown in Fig. 3 basically unchanged.

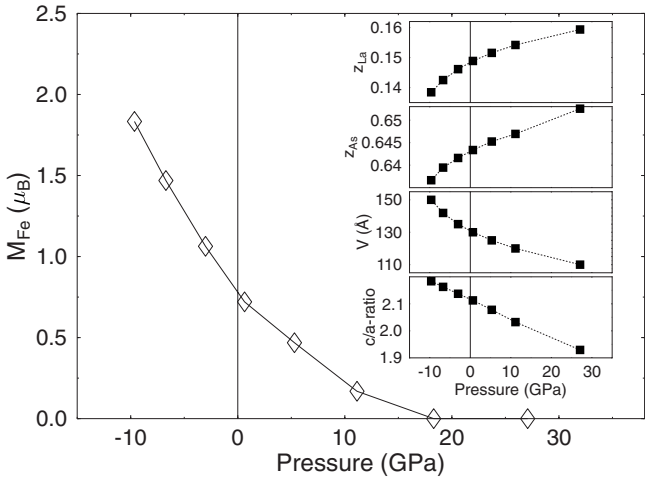

FIG. 3. Fe moment as a function of pressure for the AF3 spin structure with optimized structural parameters. The inset shows the variation in c/a, V, z_{As}, and z_{La} with pressure.

IV. DISCUSSION

The result of our study shown in Figs. 2 and 3 predicts that LaFeAsO is close to a magnetic instability. At a pressure of about 5 GPa, the Fe moment calculated within LSDA coincides with the one observed in experiments. This means that LaFeAsO is on the right side of the transition shown in Fig. 3. A strong increase in the Fe moment would be expected for negative pressure conditions, which are of course not straightforward to realize in experiments. However, it is well known that hydrogenation can lead to a sizable increase in the volume and could thus serve as a medium to simulate negative pressure for LaFeAsO. Since the electronic structure of different iron arsenide compounds is quite similar,[27] we would also expect that the behavior we found in LaFeAsO can be observed in other iron arsenide compounds.

Recently, further studies[28–30] on the magnetic properties of iron arsenide compounds under pressure were reported, which support our interpretation. Kumar *et al.*[28] performed a combined theoretical and experimental investigation for $SrFe_2As_2$. In their LSDA calculations, they find a suppression of the magnetism at a critical pressure of about 10 GPa, which is slightly higher than the critical pressure extrapolated from experiments of 4–5 GPa. Yildirim[29] performed GGA pseudopotential calculations for $CaFe_2As_2$ and LaFeAsO under pressure. His calculations for $CaFe_2As_2$ show a suppression of the Fe magnetic moment around 10 GPa (note, however, that $CaFe_2As_2$ is special due to the presence of a collapsed tetragonal phase). In the case of LaFeAsO, the Fe moment calculated within the GGA pseudopotential approach is higher at ambient pressure than

in our LSDA calculations and remains close to $2\mu_B$ up to 10 GPa but drops to zero at 20 GPa. However, the data shown do not allow one to judge if the transition is smooth as in our calculations or if a sudden collapse of the moments under pressure occurs. Finally, Xie *et al.*[30] performed calculations for $BaFe_2As_2$ under pressure and found a suppression of the Fe moment around 13 GPa.

An explanation of the magnetism in LaFeAsO in terms of localized magnetic moments is difficult, if not impossible. First, the magnetic moments are soft and depend on the spin arrangement and structural details, which is not compatible with a simple Heisenberg model. Second, the total bandwidth of the Fe $3d$ states amounts to about 7 eV. Near the Fermi energy, all five d orbitals contribute to the density of states (DOS), with little admixture of As $4p$ states. In localized systems, crystal-field splittings are a valuable tool to predict the spin state.[31,32] The related crystal-field splittings of the Fe $3d$ states in LaFeAsO (evaluated from the center of gravity of the corresponding partial DOS) are well below 0.5 eV and thus much smaller than the bandwidth.

In an itinerant magnet such as LaFeAsO,[33] the magnetic state is determined by a delicate balance between kinetic energy (favoring a nonmagnetic state) and the gain in exchange energy by spin polarization. With increasing pressure, the bands of LaFeAsO are broadened and weight is shifted away from the Fermi energy. A (rough) quantitative measure for this shift can be obtained from the integrated partial DOS weighted with a Gaussian around the Fermi energy,[34] which yields a 20–30 % reduction from −10 to +10 GPa, where the Fe moment essentially drops from $2\mu_B$ to almost 0. We do not observe abrupt changes in the electronic structure in this pressure range, consistent with the smooth (but rapid) decrease of the Fe moment in Fig. 3. However, close to the magnetic instability, the observed changes are sufficient to alter the magnetic state.

Mazin *et al.*[35] pointed out that the stripelike spin arrangement is stabilized by nesting features in the paramagnetic FS. This is confirmed by our calculations, which also show that the related nesting features remain robust under pressure. The FS consists of five sheets, with two cylindrical hole sheets around Γ and two cylindrical electron sheets around M, nested by a vector $\mathbf{Q}=(\pi,\pi,0)$. In addition, there is a hole pocket around Z, whose shape depends strongly on structural details.[36] The larger one of the Γ-centered FS sheets becomes more three dimensional around 10 GPa, but the topology of the Fermi surface does not change up to pressures of at least 10 GPa, and also the nesting features are surprisingly robust (Fig. 4). The nesting is never perfect but remains substantial throughout the considered pressure range, which explains the relative stability of the magnetism in the AF3 structure.

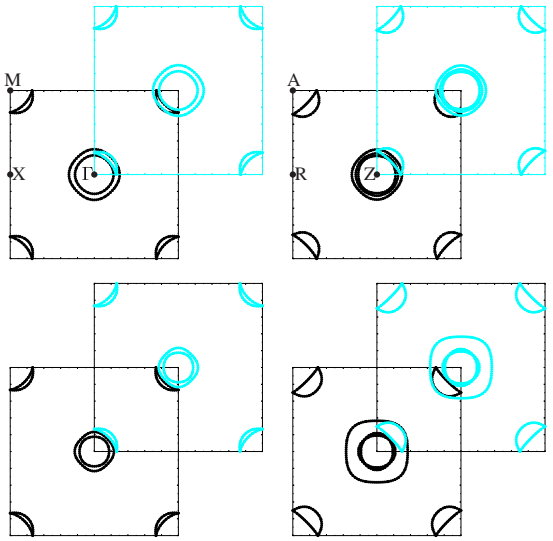

FIG. 4. (Color online) Cuts through the FS of LaFeAsO for two different volumes (top: $V=141.9$ Å^3; bottom: $V=120$ Å^3). Cuts perpendicular to the c axis in the Γ plane (left) and in the Z plane (right) are shown. To visualize nesting, the same cuts shifted by $\mathbf{Q}=(\pi,\pi,0)$ are also drawn (light color). Similar nesting is observed throughout Γ-Z.

V. CONCLUSIONS

In summary we have shown that LaFeAsO is close to a magnetic instability, which explains the discrepancies between the values for the Fe moment found in experiment and DFT calculations. On the basis of our calculations we expect a strong increase in the Fe moment with increasing volume, which could be realized, for example, by hydrogenation. The Fermi-surface topology and the reported nesting properties are fairly robust up to pressures of at least 10 GPa.

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